## Identification of Gravity-Related Effects on Crystal Growth from Melts with an Immiscibility Gap

M. Kassemi<sup>1</sup>, A. Sayir<sup>2</sup>, S. Farmer<sup>3</sup>

- <sup>1</sup> NCMR, NASA Lewis Research Center, Cleveland, Ohio
- <sup>2</sup> Case Western Reserve University, Cleveland, Ohio
- <sup>3</sup> NASA Lewis Research Center, Čleveland, Ohio

This work involves an experimental-numerical effort to study the effects of natural and Marangoni convections on solidification of single crystals from a silicate melt with a liquid-liquid immiscibility gap. Industrial use of crystals grown from silicate melts is becoming increasingly important in electronic, optical, and high temperature structural applications. Even the simplest silicate systems like  $Al_2O_3$ .  $SiO_2$  have had, and will continue to have, a significant role in the development of traditional and advanced ceramics. A unique feature of crystals grown from the silicate systems is their outstanding linear electro-optic properties. They also exhibit exceptionally high optical rotativity. As a result, these crystals are attractive materials for dielectric, optical, and microwave applications.

Experimental work in our laboratory has indicated that directional solidification of a single crystal mullite appears to be preceded by melt segregation. Disruption of the segregated state results in crystallization of a two phase structure. There is also evidence that mixing in the melt caused by density-driven convection can significantly affect the immiscibility of the liquid and result in different crystalline forms (stable or metastable crystalline phases; polycrystals or single crystals). On earth, the immiscible state has only been observed for small diameter crystals grown in float zone systems where natural convection is almost negligible. Therefore, it is anticipated that growth of large single crystals from silicate melts would benefit from microgravity conditions because of the reduction of the natural convective mixing. The main objective of this work is to determine the necessary conditions for growing superior quality single crystals from the phase separated melt by isolating the effects of convection and the other interacting transport processes.

Very little work has been done or published with regard to solidification from immiscible liquids. In this work, we study the role of gravity-driven convection on growth of single crystal mullites from the melt using hand-in-hand numerical modeling and experiments. High resolution digital images obtained in our laboratories at NASA Lewis Research Center demonstrate that mullite formation is preceded by a state of liquid-liquid immiscibility. To our knowledge, this is the first direct experimental evidence of liquid immiscibility reported for this system. Experimental results also reveal that mixing in the melt caused by density-driven convection can significantly affect the immiscibility of the liquid and result in different crystalline forms (stable or metastable crystalline phases; polycrystals or single crystals). The transport processes affecting concentration and temperature gradients in the melt and in the growing solid are quite complicated for silicate systems. The immiscibility of the liquid, segregation of dopant, and interface shape are not only directly affected by density-driven and surface-tension-driven convection in the melt but are also indirectly influenced by a significant amount of radiation and conduction heat transfer through the semi-transparent solid. The interaction between the various transport processes are further complicated by the observed multi-layered fluid structure which brings about various mechanical and thermal couplings across the liquid-liquid interface. Consequently, determination of the necessary conditions for growing superior quality single crystals from phase separated melts is not an easy task and requires isolating the effects of the various interacting transport processes.

As a first step towards gaining the necessary insight into the physical phenomena governing growth of mullites from melt, under the conditions proposed in this research effort, a series of tests

were run with an existing float-zone setup to determine the physical nature and characteristics of the melt during growth. From visual observations recorded on video, it is clear that at the desired composition, growth occurs from a melt with two distinct phase-separated regions. Preliminary evidence suggests that the viscosity of the encapsulated region (near the source) is quite higher than the viscosity of the liquid adjacent to the crystal. Additional tests are underway to further clarify the nature and composition of the two phases. These include a new experimental matrix based on specific dopant concentrations to study the effects of melt viscosity. The effect of density-driven convection on the liquid-liquid immiscibility is also experimentally investigated in a continuing series of tests by growing crystals over a wide range of diameters (from 100 microns to 1 cm). This allows us to vary the intensity of natural convection by several orders of magnitude. The effect of surface tension forces is studied by varying the Al/Si concentration of the materials and through dopant additions. The impact of thermal radiation on the liquid-solid interface shape and on the degree of homogenization in the melt will be studied in future tests by changing the dopant concentration (at fixed Al/Si compositions) which directly alters the transparency of the material. Finally, the type and quality of crystal produced (void formation, ordering, dislocation density, and low angle grain boundaries) will be characterized using scanning electron, transmission electron, and atomic force microscopy. The crystal characteristics will be correlated to the growth conditions and their effect on the transport processes.

A comprehensive numerical model is under development which ultimately will include the simultaneous effects of natural and Marangoni convection, moving boundaries, phase separated melt region, and semi-transparent radiation heat transfer in the solid. Currently, the numerical model is focused on the interaction between natural and thermocapillary convection with in the melt region and is used in conjunction with the experimental results to isolate the effect of the interacting convective mechanisms during the float-zone growth process. At this stage, the model includes the effects of natural convection, thermocapillary convection, evaporation of silica at the free surface, solutal rejection at the solid-liquid interfaces, and deformable liquid-air free surfaces. Preliminary steady state simulations predict the experimentally observed shape of the melt region correctly. They also indicate that the concentration field drastically changes as buoyancy-driven convection dominates over the surface tension-driven flow for larger diameter crystals. These results seem to indicate that, under 1-g conditions, the phase separated liquid regions may only co-exist for smaller diameter crystals where natural convection mixing effects are minimal. To confirm these findings rigorously, work is underway to use an energy-based phase field method. The phase field approach together with the Navier Stokes equations provides a continuum surface tension model that can be used to focus on the interactions between the multi-component fluid system created by the liquid-liquid immiscibility gap in the melt.